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Review

Low Temperature Preparation of Oxide Glasses and Ceramics from Metal Alkoxide Solutions

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Recent progress in low temperature synthesis of glasses and ceramics from metal alkoxide solutions has been reviewed. In this method metal alkoxide solutions are geled through hydrolysis-polycondensation and converted to glasses and ceramics by heating at relatively low temperatures. Conditions for direct preparation of bulk bodies, fibers and coating films have been described. It has been shown that fibers can be drawn when linear polymers are formed in the course of hydrolysis.

KEY WORDS: Low temperature preparation/ Oxide glasses/ Metal alkoxide/ Gelation/ Fiber/ Coating film/ Hydrolysis/ Polycondensation/

I INTRODUCTION

Metal alkoxides in solution are hydrolyzed by water and are polycondensed, producing siloxane polymers or colloidal polymeric particles. The sols thus formed are solidified as gels upon further progress of the hydrolysis-polycondensation reaction. Heating of the gels up to a temperature ranging from about 400°C to 1000°C gives oxide glasses. This alkoxide method of producing glasses is a kind of sol-gel techniques, because glass is made through the sol and gel states. This is also called non-melting technique, because glass is produced without melting of powder raw materials. The use of low temperature reactions like hydrolysis and polycondensation gives the name "low temperature synthesis of glass". This method is also used for producing ceramics directly from gel or from gel-derived glasses.

Considerable amounts of water, alcohol and organic residues have to go out of the system in the course of gel and glass formation. The resulting marked contraction of the volume may easily cause cracks and fissures, which makes the production of large window panes and bottles very difficult at present. Glass products which can be easily made by this method may be plates of $40 \times 100 \times 100$ mm^3 at the largest and cylinders of 10 mm in diameter and 100 mm in length. However, this method is characterized by the possible formation of glasses of new compositions which could not be formed by the ordinary melting method.

As to the fiber products, drawing gel fibers for producing glass fibers can be carried out at room temperature, which is in contrast with ordinary glass fiber drawing made at high temperatures ranging from 1200°C to 1400°C.

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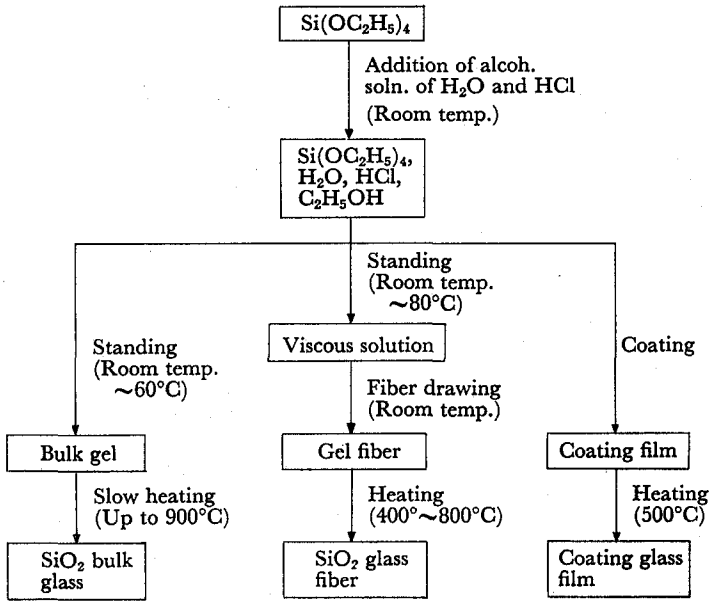
Further, this method can be applied to coating of metals, ceramics, glasses and plastics with glass and ceramic films at relatively low temperatures.

Dislich[1] prepared glass bodies by this method for the first time. He produced transparent glass discs by hot-pressing gel powders near glass transition temperature which were prepared through hydrolysis-polycondensation of metal alkoxides. Since then, Sakka and his colleagues and other investigators have been studying on the production of shaped glasses directly from metal alkoxide solutions without employing hot pressing. Attentions have been paid to adjusting the composition of starting alkoxide solutions and the condition of gelation. The results have been reviewed by Sakka in 1980[2] and 1982[3].

This paper has been written in order to review the metal alkoxide method in preparing oxide glasses and ceramics on the basis of the recent results obtained by the author's group. The problems discussed in the present paper include the outline of the alkoxide method, conditions required for preparing bulk and fiber glasses by the alkoxide method, the shapes of alkoxide polymers formed in the course of hydrolysis-polycondensation reaction and the formation of coating films from the metal alkoxide solution.

II OUTLINE OF THE METAL ALKOXIDE METHOD

The overal process of preparing bulk bodies, fibers and coating films by the alkoxide method is illustrated by the block diagrams in Fig. 1. This is based on



an example in which various forms silica glass are made from tetraethoxysilane (TEOS). In order to cause hydrolysis, an alcoholic solution of water and acid is added to the alcoholic solution of TEOS under stirring. Thus the starting solution, a

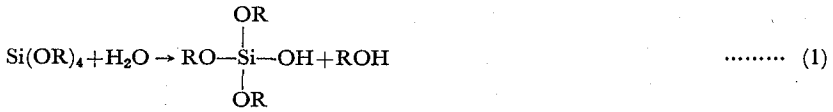
mixture of an alkoxide, water and acid in alcohol, is prepared. In the case of coating films, a substrate is dipped into the solution immediately after its preparation and withdrawn upwards, so that the hydrolysis might proceed in air after the application. In the case of bulk and fiber glasses, the alcoholic solution is kept open in air so that volatile products might be able to quit the reaction system. This leads to the formation of polymers with ≡Si-O-Si≡ bondings as a result of hydrolysis and polycondensation of the metal alkoxides. The resultant sol is solidified as a gel. Heating of a geled mass may give a bulk glass. Fibers drawn from the viscous solution immediately before its gelation become glass fibers on heating up to temperatures ranging from 400°C to 800°C, depending on the composition of glass.

Pertinent conditions have to be obeyed, however, for the successful formation of each of bulk body, fiber and coating film. The concentration of water in the starting alkoxide solution may be one of the most important factors, as shown later. The mechanism and kinetics of hydrolysis and polycondensation reactions in the alkoxide solution and the shape of polymers or particles occurring during the reaction are not well elucidated yet, although some attempts to find the mechanism have been started.[4,5]

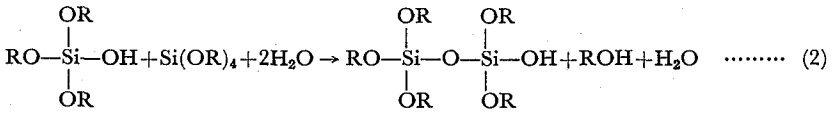
Figure 2 shows assumed formulae for the processes leading to the formation of polymers and particles in the hydrolysis and polycondensation of TEOS molecules. Figure 2 (a) corresponds to the case where a relatively less amount of water is employed. Hydrolysis of a TEOS molecule changes one of the four OR groups into OH group and separates an alcohol (ROH) molecule, as expressed by eq. (1). Equation (2) shows that another TEOS molecule hydrolyzed similarly reacts with the molecule containing one OH group to form a dimer which also contains one OH group. In this process, two H_2O molecules are consumed in the hydrolysis and one H_2O molecule is separated to form an ≡Si-O-Si≡ bonding, resulting in the net consumption of one H_2O molecule. A dimer becomes a trimer according to eq. (3). Further progress of polymerization leads to an n-mer as shown in eq. (4). The net reaction (5) given by combining eqs. (1)—(4) indicates that formation of a linear polymer requires one mol water per one mol TEOS.

Formulae given in Fig. 2 (b) have been proposed by Yoldas[6]. Hydrolysis is expressed by eq. (6) and polymerization leading to a dimer is expressed by eq. (7). If some of the OR groups bonding to Si are assumed to be hydrolyzed, then the reaction expressed by eq. (8) may occur. Yoldas assumed that when linear polymers of sufficiently high molecular weights are formed, the hydrolysis should largely progress so that all the OR groups might be hydrolyzed to OH groups as expressed by eq. (9). If this is true, three H_2O molecules per one TEOS molecule would be required for a large n value. It will be reasonable to assume that in linear polymers formed in real alkoxide solutions, side groups may be partially OR's and partially OH's. Figure 2 (c) shows formulae applied to the cases when colloidal particles are formed instead of linear polymers or when linear polymers once formed become three-dimensionally polymerized products as a result of an extreme progress of the reaction. This happens naturally when the gels are kept in air for a long time or

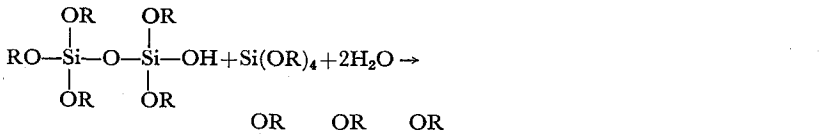
a. Formation of linear polymers



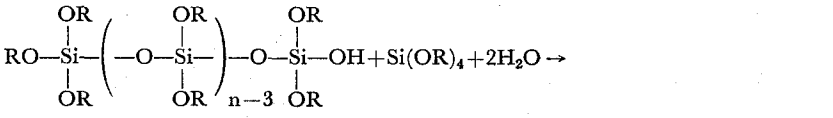
$$Si(OR)_4+H_2O \rightarrow RO-Si(OR)_2-OH+ROH \quad \cdots\cdots (1)$$



$$RO-Si(OR)_2-OH+Si(OR)_4+2H_2O \rightarrow RO-Si(OR)_2-O-Si(OR)_2-OH+ROH+H_2O \quad \cdots\cdots (2)$$

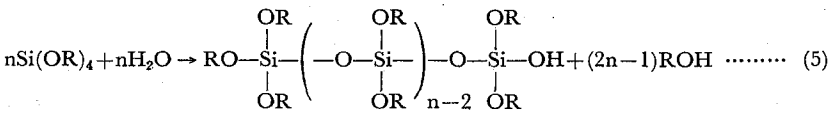


$$RO-Si(OR)_2-O-Si(OR)_2-OH+Si(OR)_4+2H_2O \rightarrow RO-Si(OR)_2-O-Si(OR)_2-O-Si(OR)_2-OH+ROH+H_2O \quad \cdots\cdots (3)$$



$$RO-Si(OR)_2-(-O-Si(OR)_2-)_{n-3}-O-Si(OR)_2-OH+Si(OR)_4+2H_2O \rightarrow RO-Si(OR)_2-(-O-Si(OR)_2-)_{n-2}-O-Si(OR)_2-OH+ROH+H_2O \quad \cdots\cdots (4)$$

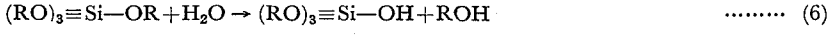
Net reaction



$$nSi(OR)_4+nH_2O \rightarrow RO-Si(OR)_2-(-O-Si(OR)_2-)_{n-2}-O-Si(OR)_2-OH+(2n-1)ROH \quad \cdots\cdots (5)$$

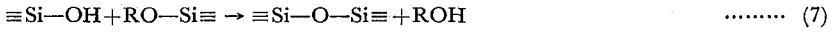
b. Formation of linear polymers (by Yoldas[6])

Hydrolysis



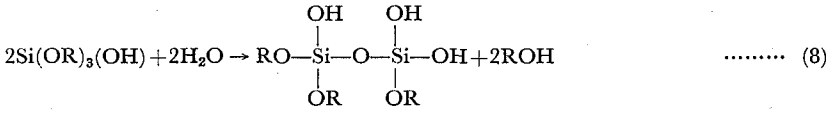
$$(RO)_3\equiv Si-OR+H_2O \rightarrow (RO)_3\equiv Si-OH+ROH \quad \cdots\cdots (6)$$

Condensation



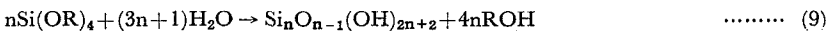
$$\equiv Si-OH+RO-Si\equiv \rightarrow \equiv Si-O-Si\equiv +ROH \quad \cdots\cdots (7)$$

Hydrolysis and condensation



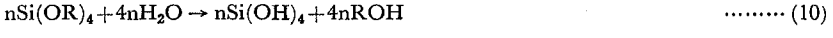
$$2Si(OR)_3(OH)+2H_2O \rightarrow RO-Si(OR)(OH)-O-Si(OR)(OH)-OH+2ROH \quad \cdots\cdots (8)$$

Linear polymers



$$nSi(OR)_4+(3n+1)H_2O \rightarrow Si_nO_{n-1}(OH)_{2n+2}+4nROH \quad \cdots\cdots (9)$$

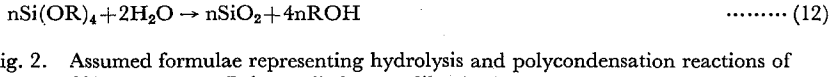
c. Formation of three dimensional SiO_2 network or particles.



$$nSi(OR)_4+4nH_2O \rightarrow nSi(OH)_4+4nROH \quad \cdots\cdots (10)$$

$$nSi(OH)_4 \rightarrow nSiO_2+2nH_2O \quad \cdots\cdots (11)$$

Net reaction



$$nSi(OR)_4+2H_2O \rightarrow nSiO_2+4nROH \quad \cdots\cdots (12)$$

Fig. 2. Assumed formulae representing hydrolysis and polycondensation reactions of $Si(OR)_4$, where R is an alkyl group like C_2H_5.

the gels are heated so that OH group may be lost. The net reaction is cxpressed by eq. (12), indicating that two H_2O molecules are required per one TEOS molecule.

It should be remembered that the above amount of water calculated for the given reactions does not control the reaction mechanism, but just gives us the idea of the necessary amount of water for the assumed reactions. Actually, linear polymers may be formed with relatively low water concentrations and three-dimensionally polymerized products are formed with relatively high water concentration[2,3], as shown later.

As hydrolysis and polycondensation progress, the alkoxide solution increases in viscosity and finally is solidified as gel. The gel consists of SiO_2 solid skeletons or agglomerated SiO_2 colloidal particles with dispersed water or air. In any case the solid part is amorphous and characterized by the irregular atomic arrangement. Heating of the gel up to a temperature between 400°C and 900°C removes water and pores, resulting in a SiO_2 glass in which the amorphous nature is kept.

The technological problem encountered in preparing bulk glasses is to avoid crack formation and fracture at gel and glass formation. For preparing glass fibers, it is important to find the composition of the starting solution which enables fiber drawing. For coating films, it is essential to create a good adhesion of the film to the substrate. The method of increasing the thickness of the film has to be worked out when necessary.

III PREPARATION OF BULK GLASSES

Volatile matters such as water, alcohol and organic residues tend to go out of the solution on gelation, drying of the gel and heating of the gel leading to the slags. In fibers and coating films the gel easily changes into glass on heating without being destroyed because of very small distances for the diffusion. In contrast, bulk

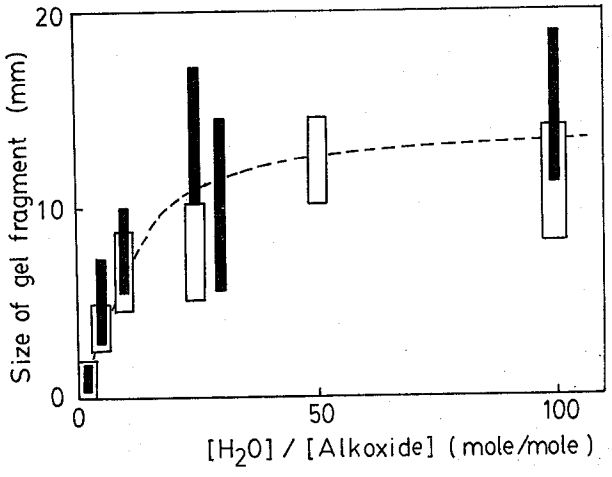


Fig. 3. Variation of the size of gel fragments for the $10TiO_2 \cdot 90SiO_2$ (wt%) glass with the water content expressed by the $[H_2O]$/Alkoxide] molar ratio.[7]

gels tend to be fractured into small pieces due to the stress in the gel body caused by the different rate of drying between the surface and inside. This difficulty has to be removed in order to prepare bulk glasses. The requirements for the formation of bulk glasses through gel from the alkoxide solution are summarized as follows.[7]

(1) The water content of the starting solution must be higher than that necessary for producing the corresponding oxide. Figure 3 shows the size of the fragments of gel used for preparing $10TiO_2$-$90SiO_2$ (wt%) glass as a function of the water content of the starting solution. It is seen that the size of fragment increases, that is, the resulting gel mass becomes large with increasing $[H_2O]/[\text{alkoxide}]$ mol ratio.

(2) The use of the container made of non-hydrophilic materials such as teflon and polystyrene is desirable, in order to avoid the adhesion and friction between the gel and the container. This prevents the occurring of cracks and fracture during the shrinkage of the gel.

(3) The heating rate should be small, in order to convert gel into glass without fracture. The higher heating rate may cause fracture due to a large internal stress in gel or explosion due to rapid expansion of remaining volatile materials.

(4) In order to convert the geled mass into glass without fracture, it is desirable to hydrolyze the alkoxide solution at higher temperatures below its boiling point.[8] Under such condition, the pores produced in the gel are large, which facilitates the vaporization of volatile substances.

The above requirements (1)～(4) are not independent from each other. Therefore, the optimum combination of the requirements have to be seeked for to make bulk glasses.

The authors prepared TiO_2-SiO_2 bulk glasses by following the above requirements.[9,10] The starting solution with the mol ratio of 50 for $[H_2O]/[Ti(OC_3H_7)_4 + Si(OC_2H_5)_4]$ was hydrolyzed at 40°C. Geled masses of rectangular rods of 20 mm×40 mm×50 mm in size and cylinders of 20 mm in diameter and 40 mm in height were obtained by hydrolysis and polycondensation. TiO_2-SiO_2 glass plates of 5 mm×20 mm×40 mm were obtained by heating the gel up to 900°C at a rate of 6°C/h.

IV PREPARATION OF FIBERS

For the preparation of glass fibers, gel fibers are drawn from the viscous alkoxide solution. The fibers are converted to glass fibers on the subsequent heating. Fibers of the systems SiO_2[10,11], SiO_2-Al_2O_3[12], SiO_2-TiO_2[10,12,13], SiO_2-ZrO_2 and SiO_2-ZrO_2-Na_2O[14,15] have been prepared in this way.

It should be noted that all starting solutions do not necessarily become drawable. The composition of the solution must be appropriate in order for the fiber drawing to be possible. Table I shows that the solution becomes spinnable when the water content for hydrolysis is low and the catalyst is acid. When the water content is high or the catalyst is alkali or ammonia, the solution becomes an elastic gel without exhibiting spinnability.

Table I. Geling characteristics of $Si(OC_2H_5)_4$ solutions of various compositions[16].

Solution	Composition of solution			Catalyst*	H_2O / $Si(OC_2H_5)_4$ (mole ratio)	Volume (cc)	content SiO_2 (g/100 cc)	Geling time (h)	Spinnability	Appearence of gel
	$Si(OC_2H_5)_4$ (g)	H_2O (g)	C_2H_5OH (g)							
1	169.5	14.7	239.7	HCl	1	510	9.61	525	Good	Transparent
2	382.0	33.0	83.4	HCl	1	550	20.1	360	Good	Transparent
3	169.5	292.8	37.5	HCl	20	500	9.8	248	No	Transporent
4	50	3.8	47.6	NH_4OH	1	118	12.2	565	No	A little turbid
5	50	7.6	47.6	NH_4OH	2	120	12.0	742	No	A little turbid

* The mole ratio $[HCl]/[Si(OC_2H_5)_4]$ or $[NH_4OH]/[Si(OC_2H_5)_4]$ is 0.01.

Figure 4 is a diagram[7] shwoing the fiber drawing behavior versus composition relationship for the formation of SiO_2 glass fibers from the starting $Si(OC_2H_5)_4$-H_2O-C_2H_5OH solutions. The ratio $[HCl]/[Si(OC_2H_5)_4]$ was kept at 0.01. The

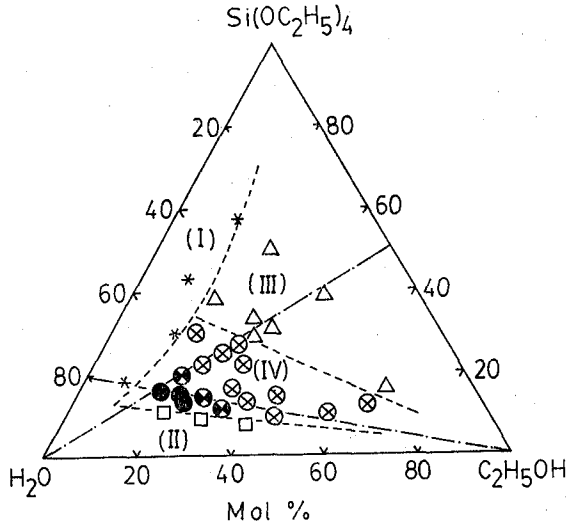


Fig. 4. Relation between fiber drawing behavior and composition of $Si(OC_2H_5)_4$-H_2O-C_2H_5OH solution with $[HCl]/[Si(OC_2H_5)_4]=0.03$ hydrolyzed at 80°C.[7]
* immiscible (area I), □ not spinnable (area II), ● not-geling (area III), ⊗ circular cross-section (area IV), non-circular cross-section (area IV), ○ circular and non-circular cross-section (area IV).

hydrolysis reaction has been carried out at 80°C. The triangular diagram can be divided into 4 areas.

The components of the solution are not miscible with each other in area I, where the C_2H_2OH content is low. In area II, where the $[H_5O]/[Si(OC_2H_5)_4]$ ratio is over 5, the solutions do not exhibit spinnability and are solidified as a jelly-like elastic gel. No gelation and spinnability are observed[17] for the solutions belonging to area III, in which the $[H_2O]/[Si(OC_2H_5)_4]$ ratio is less than 1.5. The

solution in area IV, in which the $[H_2O]/[Si(OC_2H_5)_4]$ ratio is 1.5～4, exhibit spinnability and fiber drawing is possible. On heating up to 500°C～900°C, the drawn gel fibers become SiO_2 glass fibers. The cross sections of the fibers thus prepared are not necessarily circular unlike the ordinary glass fibers drawn through a nozzle from the high temperature melt.[7] The compositions giving a circular cross-section are very limited; non-circular cross-sections occur in most of area IV.

Figure 5 (a) shows the dependence of the cross-section on the water content

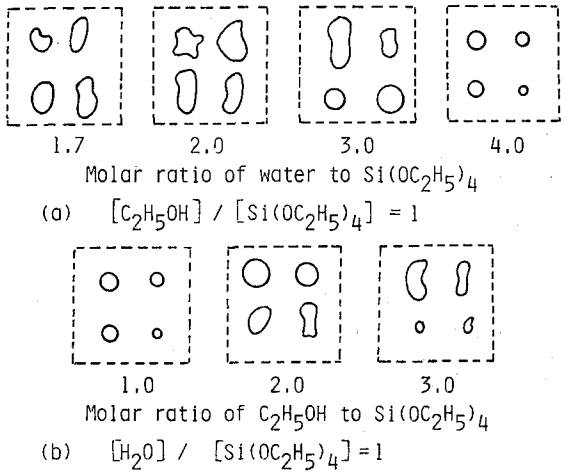


Fig. 5. Schematic representation showing the change of the shape of cross-section of SiO_2 fibers with the composition of the starting $Si(OC_2H_5)_4$ solution.[7]
(a) Change with the water content at a molar ratio of C_2H_5OH to $Si(OC_2H_5)_4$ being unity.
(b) Change with the C_2H_5OH content at a molar ratio of water to $Si(OC_2H_5)_4$ being four.

of the starting solution. Solutions with high $[H_2O]/[Si(OC_2H_5)_4]$ ratio of 4 give the circular cross-section. Figure 5 (b) shows the dependence of the cross-section on the C_2H_5OH content, indicating that the circular cross-section can be found from the solutions with low C_2H_5OH content.

The reason for the non-circular cross-section has been discussed by measuring the volume change of the $Si(OC_2H_5)_4$ solution on sol-gel conversion. Figure 6 shows the relative volume decrease observed for the process from the moment of fiber drawing to the time when the volume change is completed as a function of the water content (Fig. 6 (a)) and C_2H_5OH content (Fig. 6 (b)). This volume decrease corresponds to the solidification or drying of drawn fibers. It is seen that the cross-section is circular when the volume decrease on solidification is small and non-circular when it is large. It is obvious that the circular circumference formed on the moment of fiber drawing cannot be kept if there is a very large decrease in the fiber volume until its solidification.

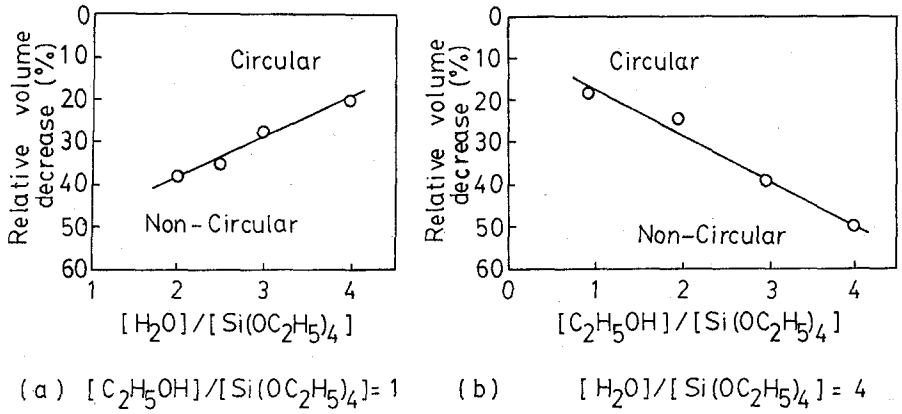


Fig. 6. Relative volume decrease of $Si(OC_2H_5)_4$ solutions on solidification of fibers as functions of the content of water (a) and C_2H_5OH (b).[7] Relative volume decrease (%)= [(Volume at fiber drawing) − (Volume observed at constant volume after drawing)]/ (Volume at fiber drawing) × 100.

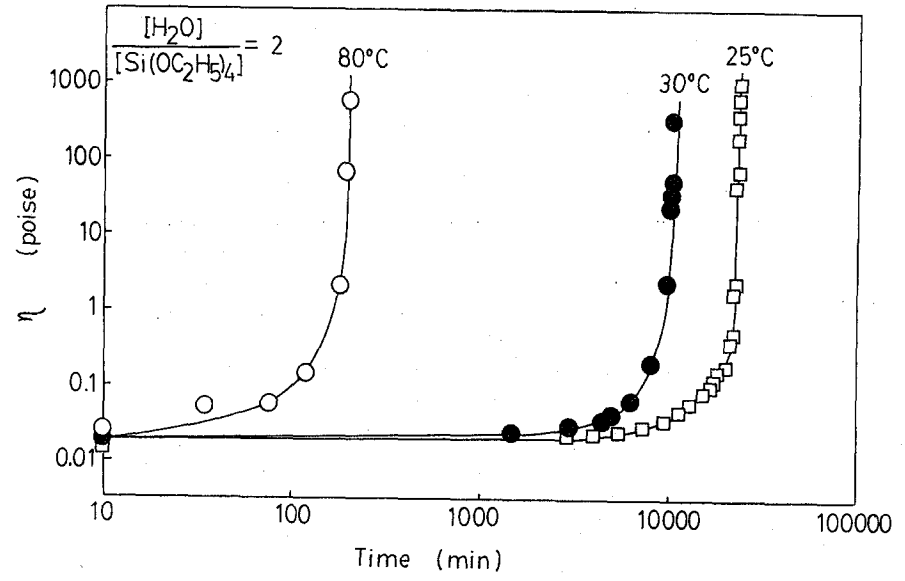


Fig. 7. Variation of the viscosity of a $Si(OC_2H_5)_4$ solution with the molar ratio $[H_2O]/[Si(OC_2H_5)_4]=2$ at 25°, 30° and 80° as a function of time.

Figure 7 shows the time change of the viscosity of a TEOS solution with the $[H_2O]/[Si(OC_2H_5)_4]$ ratio being 2 for three different temperatures.[7] It is catalyzed by hydrochloric acid. The viscosity increases with time as the hydrolysis-polycondensation reaction increases. When the viscosity reaches about 10 poise, the solution becomes sticky and spinnable, which makes it possible to draw fibers. Fiber can be drawn by immersing a glass rod in the solution and pulling it up. It is seen from Fig. 7 that the time required for the solution to reach the drawable state is shorter for higher reaction temperatures. At 80°C only about two hours

are needed until the solution becomes drawable.[17] About two hours may be reasonable for the application of the alkoxide method to the practical production.

Another requirement for the practical application is that the length of time during which fibers can be drawn continually should be long. This possibility has been found by examining the time dependence of viscosity for the alkoxide solutions of different water contents shown in Fig. 8. The reaction temperature has

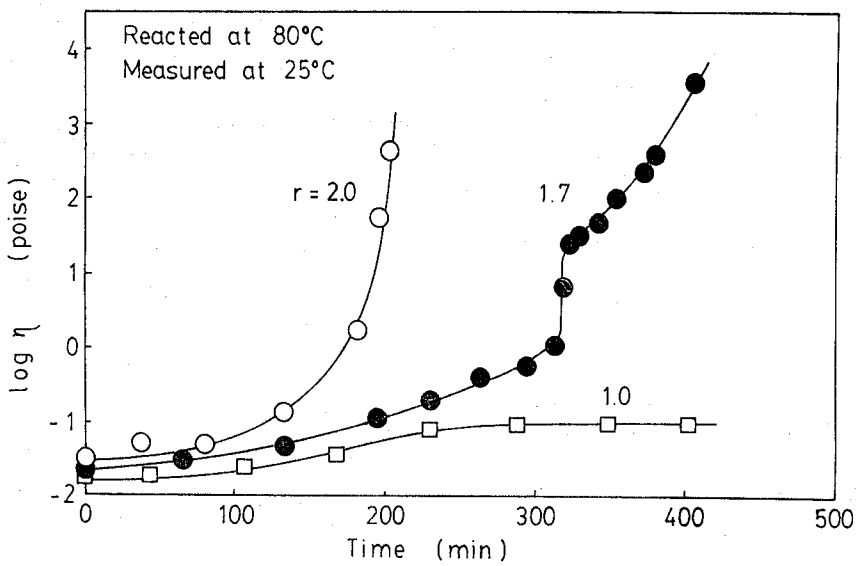


Fig. 8. Change of viscosity of $Si(OC_2H_5)_4$-H_2O-C_2H_5OH solution at 80°C. r= $[H_2O]/[Si(OC_2H_5)_4]$.

been 80°C, while the measurement of viscosity has been made at 25°C. It is seen in Fig. 8 that in the solution with the $[H_2O]/[Si(OC_2H_5)_4]=1.7$, the increasing rate of the viscosity markedly decreases after the viscosity reaches about 10 poises. This is interpreted to be caused by the exhaustion of the water in the solution for the hydrolysis reaction. Accordingly, it is possible to continue drawing for a prolonged time. Actually, the viscosity of the solution continues to increase. This happens because the hydrolysis-polycondensation reaction proceeds by the absorption of moisture from air at 80°C. The cooling of the solution to room temperature or lower temperatures at the time when the solution has become drawable is effective in prolonging the time available for drawing.

V PROCESS OF HYDROLYSIS AND POLYCONDENSATION

In the previous section it has been shown that the lower water content of the alkoxide solution is favorable for fiber drawing, while the higher water content is effective in making a bulk gel and glass, although no spinnable state appears in this case. The latter fact has been confirmed by a number of investigators.[18,19]

Sakka and his colleagues assumed that linear polymers are formed in the low

water content solutions which show spinnability on the way of progressing hydrolysis-polycondensation reaction. It was also assumed that three-dimensional networks or colloidal particles may be formed in the high water content solutions which show an elastic nature before gelation and no spinnability.

In order to confirm these, the molecular weights and intrinsic viscosities of the solutions taken in the course of gelation of the TEOS solutions have been measured and discussed in terms of the shape of the polymers produced in the solutions.[20]

The compositions of the solutions used in the measurement are shown in Table II. Solutions 1 and 2 are characterized by the lower water contents, solution 3

Table II. Compositions and properties of $Si(OC_2H_5)_4$ solutions.

Solution*	$Si(OC_2H_5)_4$ (g)	H_2O r**	C_2H_5OH (ml)	Concentration of SiO_2 (wt%)	Spinnability	Time for gelling (h)
1	169.5	1.0	324	33.3	Yes	233
2	178.6	2.0	280	42.3	Yes	240
3	280.0	5.0	79	61.0	No	64
4	169.5	20.0	47	33.5	No	138

* The ratio $[HCl]/[Si(OC_2H_5)_4]$ is 0.01 for all glasses.

** r is expresses the ratio $[H_2O]/[Si(OC_2H_5)_4]$.

by the intermediate content and solution 4 by the higher water content. The solutions have been kept at 30°C for the hydrolysis-polycondensation reaction. A portion of the solution has been taken at various times in the course of the reaction. The silicon alkoxide polymers in the solution have been trimethylsilylated for stabilization, dissolved in benzene and subjected to the measurement of molecular weight and viscosity. The number average molecular weight M_n was estimated from the freezing point depression ΔT_f of the benzene solution of the alkoxide polymers using the formula,

$$M_n = K_f \cdot 1000 \cdot g/(G \cdot \Delta T_f) \tag{13}$$

Here, g is the weight of trimethylsilylated polymers, G is the weight of benzene and K_f is 5.12, a freezing point depression constant of benzene. In order to estimate the intrinsic viscosity $[\eta]$, the relative viscosities η_{rel} of the trimethylsilylated alkoxide polymers have been measured by an Ostwald viscometer at 25°±0.02°C in the concentration range from 1 g/dl to 10 g/dl as a function of the concentration C. The values of η_{rel} have been converted to the specific viscosities η_{sp} $(=\eta_{rel}-1)$ and then to the reduced viscosities η_{sp}/C. The values of $[\eta]$ have been estimated by extrapolating the $\eta_{sp}/C \sim C$ plot to the $C=0$ axis.

Figure 9 shows the variation of M_n with the reduced reaction time t/t_g, where t_g is the geling time. Figure 10 shows the $\eta_{sp}/C \sim C$ plots for the alkoxide polymers taken from solution 1 at various reaction times. The numbers attached to the lines in the figure denote the measured value of M_n. It is seen that the slopes of

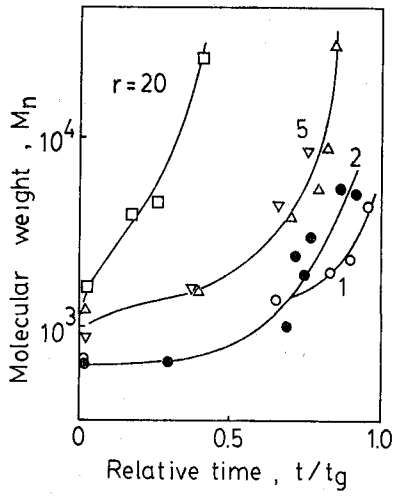


Fig. 9

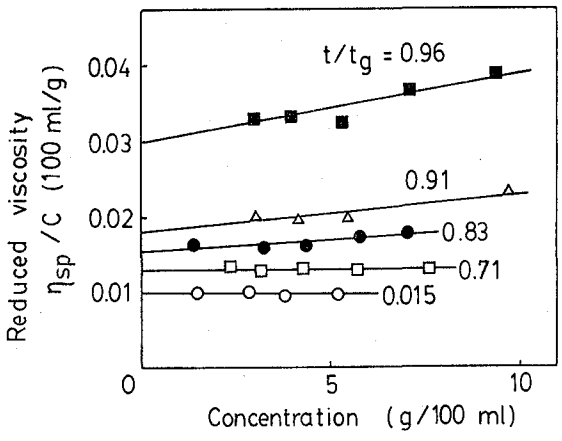


Fig. 10

Fig. 9. Change of number-average molecular weight M_n of the trimethylsilylated alkoxide polymers with relative time (t/t_g (t_g is the geling time) for $Si(OC_2H_5)_4$ solutions with different r's. The marks △ and ▽ for the solutions with r of 5.0 correspond to the polymers trimethylsilylated with trimethylchlorosilane (TMC) and hexamethyldisiloxane (HMDS), respectively.

Fig. 10. Relations between reduced viscosity η_{sp}/c and concentration of the trimethylsilylated alkoxide polymers for solution 1 with r of 1.0.

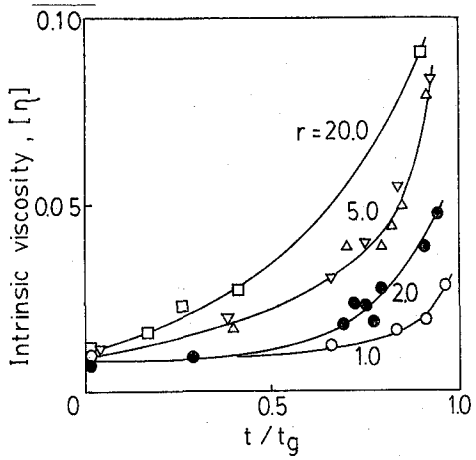


Fig. 11. Change of intrinsic viscosity [η] with relative time t/t_g for $Si(OC_2/H_5)_4$solutions with different r's.

the straight lines and the values of [η] are larger for larger M_n values. The occurrence of the slope in the lines indicates that linear polymers are found in the solution.[16] Figure 11 shows the variation of [η] with t/t_g.

Figure 12 shows the log M_n versus log [η] plots. The slope of the plot is larger than 0.5, that is, 0.75 and 0.64 respectively for solutions 1 and 2 of which the water content is low. It is smaller than 0.5, that is, 0.34 for solution 4 of which the water

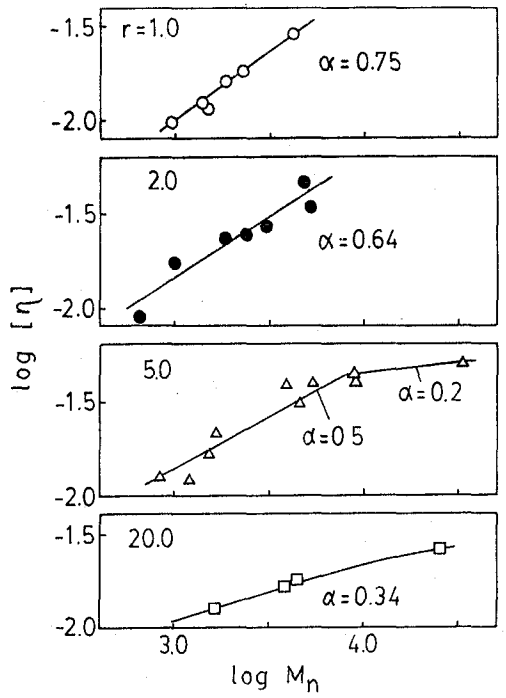


Fig. 12. Relation between M_n and $[\eta]$ of the trimethylsilylated alkoxide polymers for $Si(OC_2H_5)_4$ solutions with different r's.

content is high. The slope for solution 3 which has the intermediate water content is about 0.5 at the early stage of the hydrolysis-polycondensation reaction and about 0.2 at the later stage.

It is known that for the polymer solutions $[\eta]$ is related to M_n by the expression.[22~24]

$$[\eta] = kM_n^{\alpha} \tag{14}$$

where k is a constant depending on the kind of the polymer, solvent and temperature. The exponent α, that is, the slope of the $\log [\eta]-\log M_n$ plot takes a value between 0~2.0. The value depends on the shape of polymers: $\alpha=0$ for rigid spheric particles, $\alpha=0.5\sim1.0$ for flexible, chainlike or linear polymers and $\alpha=1.0\sim2.0$ for non-flexible or rigid, rod-like polymers.[24] It is reported for high polymers containing siloxane bondings $\equiv$Si-O-Si$\equiv$ that $\alpha=0.5$ for linear polydimethylsiloxanes, $\alpha=0.21\sim0.28$ for branched or crosslinked polymethylsiloxanes and $\alpha=0.3$ for spheric polysilicates.[25]

Referring to these, the present experimental results on the $[\eta]\sim M_n^{\alpha}$ relationships can be interpreted to show the followings. In solution 1 with $r=[H_2O]/[Si(OC_2H_5)_4]$ equaling 1.0, the alkoxide polymers grow as linear polymers with increasing molecular weight, that is, linear polymers are formed in the solution. Linear

polymers are also found in solution 2 with $r=2.0$. Solution 3 with $r=5.0$ contains linear polymers at the early stage of the reaction but three-dimensional or spheric growth of polymers occurs at the later reaction stage close to the onset of gelation. In solution 4 containing a much amount of water expressed by $r=20$, three-dimensional or spheric growth of alkoxide polymers are predominant.

The above results are summarized in Table III. Linear polymers are main

Table III. The exponent α's for the alkoxide polymers, properties of $Si(OC_2H_5)_4$ solutions and shape of the resultant glasses.

Solution	H_2O / r	α	Type of polymer	Spinnability	Shape of the glasses	
					Fiber	Bulk
1	1.0	0.75	Linear	Yes	Yes	No
2	2.0	0.64	Linear	Yes	Yes	No
3	5.0	0.5	Branched	No	No	No
		0.2	Three-dimensional			
4	20.0	0.34	Three-dimensional Spherical	No	No	Yes

reaction products in solutions 1 and 2 which become drawable. Three-dimensional polymers or particles are dominant in solution 4 which does not show spinnability but form a large bulk gel and glass. Solution 3 is intermediate between the above two cases, resulting in no drawability and no bulk gel formation. This systematic conclusion may prove the author's prediction that the fiber drawing is only possible for the alkoxide solutions containing linear polymers.[2,3]

VI PREPARATION OF COATING FILMS

Dip coating of metals, plastics, glass and ceramics with essentially inorganic films by using metal alkoxide solutions as starting solutions is attracting much attention. This technique can give the substrate a new function or improve it surface characteristics. Dip coating enables to coat the substrate at relatively low temperatures. Also it can be easily applied to a very large surface compared with sputtering and other vapor deposition techniques. This is especially important for non-flexible substrates such as sheet and plate glasses and thick metal plates.

The dip coating technique was developed by Schroeder[26,27] and his colleagues around 1960 to provide glasses and plastics with special optical characteristics. These days this technique is employed in giving the substrate useful optical and electrical properties such as antireflection[28] and electrical conductivity.[29,30]

Preparation of coating films using metal alkoxide solutions is characterized by the following features different from the preparation of fibers and bulk bodies mentioned earlier.

(1) Very small film thickness. A very thin film of 0.05～0.2 μm in thickness can be made by one coating run consisting of dipping, withdrawal and heating. A whole process has to be repeated to make thicker films.

(2) Use of diluted solutions. Relatively diluted solutions have to be employed

in order to obtain uniform coating films which firmly adhere to the substrate.

(3) Application of solutions at low viscosities. The substrate is dipped in alkoxide solutions having a low viscosity ranging from 1 to 6 centipoise. This range of viscosity is very low compared with the viscosities of more than 10 poises suitable for fiber drawing.

(4) Importance of adhesion of the coating film to the substrate. Most of defects in coating process are caused by poor adhesion between coating film and the substrate. It should be recalled that the adhesion of the alkoxide solution or gel with the container is not desirable in making fibers and bulk bodies.

These and other points to be considered in preparing coating films will be discussed on the basis of the examples of SiO_2, $BaTiO_2$ and transition metal oxide-SiO_2 coating films.

1. SiO_2 coating film

Coating of soda-lime silica glasses with SiO_2 is expected to increase their chemical resistance to acid, suppress the diffusion of sodium out of them and increase their scratch hardness. Schroeder et al.[26] made SiO_2 coating films 0.05～0.15 μm thick by the dip coating technique. The present author and his colleagues[31] investigated how to increase the thickness of the film.

A microscope slide of soda-lime silica glass has been dipped in TEOS solutions with the $[H_2O]/[Si(OC_2H_5)_4]$ ratio being 11 at 1.5—2 centipoises in viscosity, withdrawn upwards at a rate of 1.67 mm/sec and heated at 500°C for 30 min. A coating film about 0.2 μm thick has resulted. In order to examine the possibility of increasing the film thickness, TEOS solutions for coating with increased viscosities have been prepared by increasing the hydrolysis-polycondensation time and by adding various amounts of hydroxypropylcellulose (abridged to hpc) known as a viscosity-increasing reagent to the solution.

Figure 13 shows the film thickness as a function of the viscosity of the solution

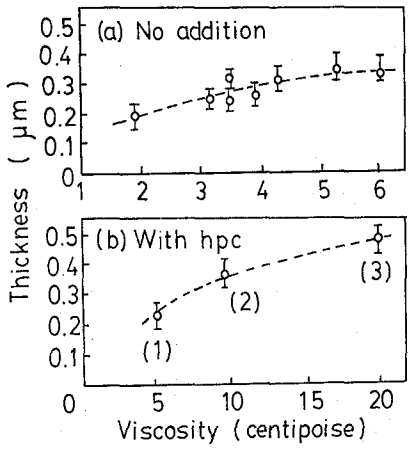


Fig. 13. Change of the thickness of SiO_2 film with the viscosity of solution in the range where a uniform coating is obtained. (a) No addition, (b) added with hydroxypropylcellulose.

for the cases in which the viscosity increases as a result of hydrolysis-polycondensation reaction (a) and as a result of addition of hpc (b). Figure 13 (a) indicates that the film thickness increases with the viscosity, reaching 0.3 μm at 6 centipoises. Beyond this viscosity, the films are deteriorated by defects such as cracks and separation from the substrate. Figure 13 (b) indicates that the film thickness increases with the viscosity, reaching 0.5 μm at 20 centipoises. When the viscosity is further increased as a result of addition of more hpc, the film exhibits cracks and separation from the substrate. Thus the upper limit of the film thickness for one run of application is 0.5 μm.

The preparation of a uniform film without defects requires the formation of strong adhesive bonds between the film and the substrate before strong cohesive bonds are formed within the film. The adhesive bondings are assumed to be formed through OH groups from both film and substrate.

2. $BaTiO_3$ coating film

Three metal alkoxide solutions E_1, E_2 and E_3 containing the metal alkoxides corresponding to 1.72, 4.28 and 6.34 wt% $BaTiO_3$, respectively, have been prepared. The compositions of the solutions are shown in Table IV. $Ba(i\text{-}OC_3H_7)_2$ has been prepared by putting Ba metal into $i\text{-}C_3H_7OH$, according to Mazdiyasni *et al.*[32]

Table IV. Composition of solutions for $BaTiO_3$ coating films.

	1	2	3
Ba metal (mol)	0.01	0.03	0.05
$Ti(OC_3H_7)_4$ (mol)	0.01	0.03	0.05
$CH_3COCH_2COCH_3$ (mol)	2.33×10^{-3}	7.00×10^{-3}	1.17×10^{-2}
H_2O (mol)	0.03	0.09	0.075
CH_3COOH (mol)	0.71	1.21	1.44
$iso\text{-}C_3H_7OH$ (ml)	100	100	100
$BaTiO_3$ (wt%)*	1.72	4.28	6.34

* Concentration calculated assuming the $BaTiO_3$ formation.

The starting $Ba(i\text{-}OC_3H_7)_2$-$Ti(i\text{-}OC_3H_7)_4$ solutions have been prepared by adding $i\text{-}C_3H_7OH$ solution of $Ti(i\text{-}OC_3H_7)_4$ and $CH_3COCH_2COCH_3$ to $Ba(i\text{-}OC_3H_7)_2$ under reflux, stirring in N_2 atmosphere at 80°C and then adding $i\text{-}C_3H_7OH$ solution of H_2O and CH_3COOH. The solutions for coating thus prepared have been yellowish and transparent.

For coating, glass or stainless steel substrates have been dipped in solutions, withdrawn upwards at a rate of 0.147～0.572 mm/sec and heated at 500°C for 10 min. Repetition of this coating process leads to an increase in the film thickness. The resultant coating films are uniform and transparent. Figure 14 shows the variation of the film thickness applied on the soda-lime-silica glass substrate with the number of applications. Linear relationships are found between the thickness and the number of applications. It is also seen that the film is thicker for solution of the higher $BaTiO_3$ concentration. It should be noted that the omission of the

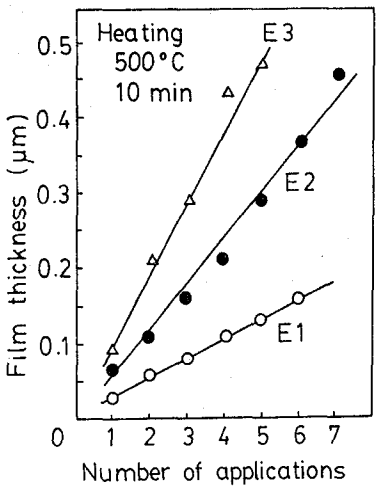


Fig. 14. Film thickness vs. number of applications for $BaTiO_3$ films by the dip-coating technique. Solution E1, E2 and E3 contain 1.72, 4.28 and 6.34 wt% $BaTiO_3$, respectively.

heating process for each run leads to defects, that is, the film may be peeled off. It can be said that heating at 500°C causes the applied film to become a part of the substrate, which assures a firm adhesion of the film to the substrate.

Figure 15 shows the effect of the rate of withdrawal on the film thickness. The thickness increases with increasing rate of withdrawal. As shown in Fig. 16, linear relationships are found for the log t-log U plots. Yang *et al.*[33] prepared coating films of styrene, hexylmethacrylate and toluol by the dip coating technique and

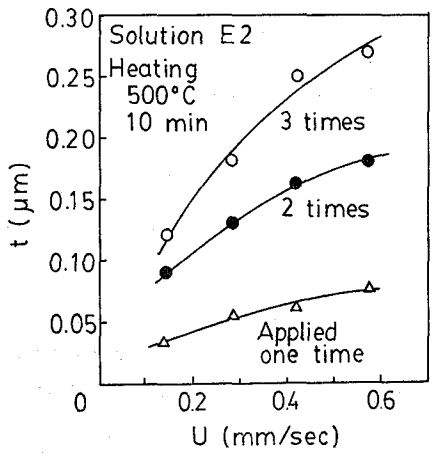


Fig. 15

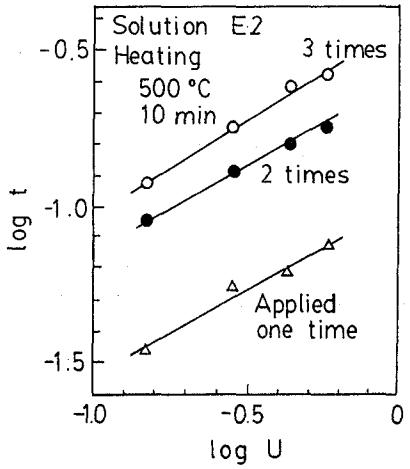


Fig. 16

Fig. 15. Change of film thickness t with the rate of withdrawal U for $BaTiO_3$ coating films.
Fig. 16. Change of film thickness t with the rate of withdrawal U for $BaTiO_3$ coating films expressed in logarithmic scale.

discussed the film thickness on the basis of the following expression.

$$t = J \cdot \xi \left(\frac{\eta - \eta_s}{\eta_0}\right)^{0.84} \left(\frac{\eta \cdot U}{g \cdot \rho_s}\right)^{1/2} \tag{15}$$

where t is the film thickness, J is a constant, ρ_s is the density of the solution, $\xi = \rho_s/\rho_p$ (ρ_s is the density of polymers), η is the viscosity of the solution, η_s is the density of the solvent, η_0 is found in the equation $\eta = \eta_s + \eta_0 C_p^{\alpha}$, where C_p is the concentration of polymers, and g is the acceleration of gravity. This equation indicates that the slope of the log t–log U plot is 1/2. Dislich and Hussmann[27] found the slope of 2/3 for the coating film prepared from alkoxide solutions. The slope of 0.52～0.62 has been observed in the present experiment on $BaTiO_3$ films.

Upon heating of the coating film, cubic $BaTiO_3$ crystals have started to precipitate at 600°C, as indicated by the x-ray diffraction pattern shown in Fig. 17.

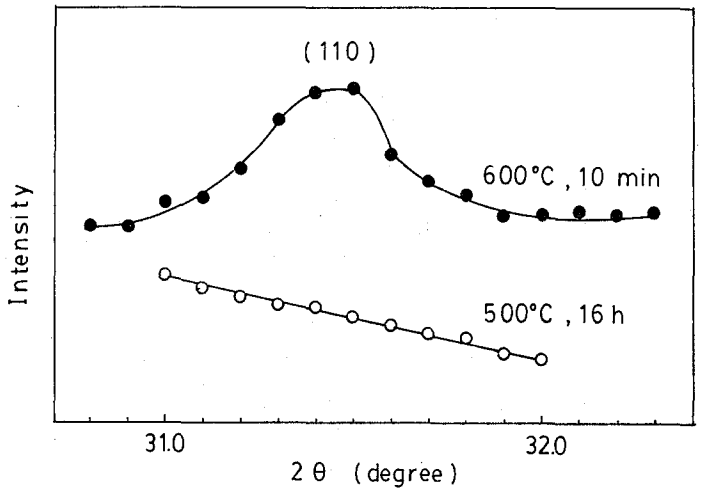


Fig. 17. X-ray diffraction patterns of coating films prepared from solution E2.

It has been found that the $BaTiO_3$ powder from the alkoxide solution of the identical composition crystallizes at a lower temperatures, that is, at 400°C. This may be attributed to the presence of more active surfaces in the powder than in the film.

Yanovskaya et al.[34] prepared $BaTiO_3$ coating films from the mixture of ethanol solution of Ba and titanium ethoxide. The coating film had to be heated in N_2 atmosphere after application, because heating in air changed the film into powder on the substrate. On the contrary, the present author's sample mentioned above could be heated in air without such a defect. This difference may be attributed to the presence of acid in the starting solution in our case. However, the effect of the acid is left to be studied.

3. Transition metal oxide-SiO_2 coating films

Dip coating of sheet glass with a colored film is expected to be very useful for producing colored window glasses. Considering that a coating film made by one

application is very thin at several tenths of a micrometer, the coating film should be quite intensely colored by containing the coloring oxide as much as several ten %. This has proved to be possible as shown below.

Starting solutions for R_mO_n-SiO_2 compositions, where R is Cr, Mn, Fe, Co, Ni and Cu, have been prepared by mixing $Si(OC_2H_5)_4$, H_2O, HCl and nitrate of a respective transition metal.[35,36] Microscope slides of soda-lime-silica glass have been dipped in these solutions, drawn upwards and heated to 500°C. Opticcl absorption of the resultant coating films 0.3～0.5 μm thick have been measured. The optical absorption spectra of the coating film consisting of CuO-SiO_2 glass are shown in Fig. 18 as typical examples. For comparison an absorption spectrum

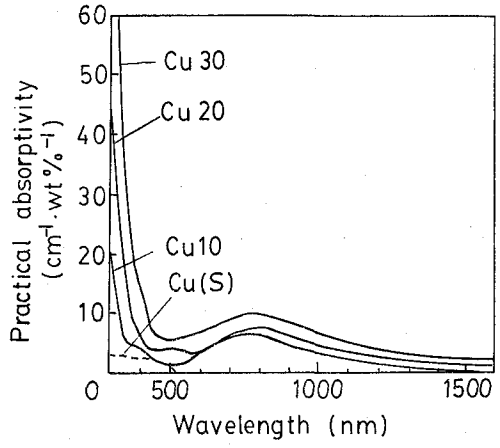


Fig. 18. Optical absorption spectra of CuO-SiO_2 films.
Cu10: CuO 10 mol%, Cu20: CuO 20 mol%,
Cu30: CuO 30 mol%, Cu(S): Schultz' data[37].

of Cu-containing SiO_2 glass measured by Schultz[37] is shown by a broken curve. This glass was prepared by the flame spray technique at high temperatures around 1800°C.

The broad bands peaking around 800 nm on the curves of alkoxy-derived glasses are attributed to octahedrally coordinated Cu^{2+} ions.[38] The spectra obtained in our study are characterized by the presence of the 800 nm bands and in a marked contrast with that of Schultz, which completely lacks in the 800 nm band. This latter fact indicates that all the Cu atoms are present Cu^+ ions which have no absorption in the visible region. It is known for Cu[39] and other transition metals in oxide glasses that when a transition metal ion can have two different valence states, the oxidation-reaction equilibrium tends to shift towards the oxidation state as equilibrated temperature decreases. This indicates that most of Cu metal ions may take the state of Cu^{2+} ions, that is, the higher valency state is realized in glasses prepared by the low temperature sol-gel synthesis.

The maximum possible content of a transition element oxide for obtaining uniform coating film has been 10 mol% for Cr_2O_3, 20 mol% for Mn_2O_3, 45 mol% for Fe_2O_3, 45 mol% for CoO, 55 mol% for NiO and 45 mol% for CuO.

These contents of transition metal oxides have produced noticeably colored coating films by one application of dip coating. The optical transmittance at 555 nm of the uniformly colored 0.2～0.5 μm thick films with the most intensive absorption was 81% for Cr, 68% for Mn, 63% for Fe, almost 0% for Co, 59% for Ni and 95% for Cu.

VII SUMMARY

The low temperature synthesis based on hydrolysis-polycondensation reaction of metal alkoxides in solution is attracting much attention as a new useful techniquee of producing special glasses and ceramics. In this article, a particular stress has been laid on the production of shaped glasses such as bulk glasses, fibers and coating films. The preparation of active powders from metal alkoxides is also important, although no mention has been made in this paper. Such powders are expected to be easily sintering starting materials for preparing new, functional glasses and ceramics. It is also possible to obtain high performance composites consisting of inorganic polymers combined with organic polymers. It should be noted, however, that the basic studies on the mechanism of hydrolysis-polycondensation reaction of metal alkoxides are left to be made, in order to accomplish further progress of this technique.

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